

Short communication

Ammonia fuel cell using doped barium cerate proton conducting solid electrolytes

L. Pelletier^{a,*}, A. McFarlan^a, N. Maffei^b

^a Natural Resources Canada, CANMET Energy Technology Centre, 1 Haanel Drive, Bells Corners Complex, Ottawa, Ont., Canada K1A 1M1

^b Materials Technology Laboratory, CANMET, Natural Resources Canada, 405 Rochester St., Ottawa, Ont., Canada K1A 0G1

Accepted 3 February 2005

Available online 31 May 2005

Abstract

Proton-conducting solid electrolytes composed of gadolinium-doped barium cerate (BCG) or gadolinium and praseodymium-doped barium cerate (BCGP) were tested in an intermediate-temperature fuel cell in which hydrogen or ammonia was directly fed. At 700 °C, BCG electrolytes with porous platinum electrodes showed essentially no loss in performance in pure hydrogen. Under direct ammonia at 700 °C, power densities were only slightly lower compared to pure hydrogen feed, yielding an optimal value of 25 mW cm⁻² at a current density of 50 mA cm⁻². This marginal difference can be attributed to a lower partial pressure of hydrogen caused by the production of nitrogen when ammonia is decomposed at the anode.

A comparative test using BCGP electrolyte showed that the doubly doped barium cerate electrolyte performed better than BCG electrolyte. Overall fuel cell performance characteristics were enhanced by approximately 40% under either hydrogen or ammonia fuels using BCGP electrolyte. At 700 °C using direct ammonia feed, power density reached 35 mW cm⁻² at a current density of approximately 75 mA cm⁻². Minimal loss of performance was noted over approximately 100 h on-stream in alternating hydrogen/ammonia fuels.

Crown Copyright © 2005 Published by Elsevier B.V. All rights reserved.

Keywords: Ammonia; Proton conductor; Doped barium cerate; Fuel cell performance

1. Introduction

Recently, alternative technologies to reduce greenhouse gas (GHG) levels generated by the transportation and power generation sectors have been explored. Hydrogen fuel cells are quite attractive since they offer the possibility to achieve zero GHG emissions. However, issues concerning hydrogen production, storage, transportation and refueling infrastructure still remain. Hydrogen carriers can help resolve some of the present challenges. Methanol, natural gas and gasoline are just a few hydrocarbon-based carriers currently considered for the transportation sector [1].

Ammonia is an inorganic hydrogen carrier which consistently ranks among the highest volume chemicals produced worldwide. Production, storage and transport of ammonia

have been optimized over the last century [1]. A comparative analysis has shown that ammonia is potentially a more attractive hydrogen carrier than methanol for fuel cells [2,3]. Hydrogen produced from ammonia in an ammonia cracker can be used to fuel alkaline fuel cells (AFC) as well as polymer electrolyte membrane (PEM) fuel cells [4,5]. In a carbon-constrained world, ammonia is one of the most economical hydrogen carriers because CO₂ is separated as a pure byproduct stream during ammonia production [6].

Farr and Vayenas [7] first reported the direct oxidation of ammonia to nitric acid with coproduction of electricity in a high temperature solid oxide fuel cell (SOFC).

Recent studies have shown the use of direct ammonia feeds for a SOFC using yttria stabilized zirconia electrolytes [8]. However, as demonstrated by Farr and Vayenas, employing ammonia directly to fuel SOFCs having oxygen ion conducting electrolytes poses a substantial risk of producing NO_x compounds.

* Corresponding author. Tel.: +1 613 947 3501; fax: +1 613 996 9400.
E-mail address: lupellet@nrcan.gc.ca (L. Pelletier).

We have recently reported an intermediate temperature direct ammonia fuel cell that uses a proton-conducting gadolinium-doped barium cerate solid electrolyte [9]. Several materials have been shown to have high proton conductivity at intermediate temperatures [10,11]. Fuel cells using these electrolyte materials prevent oxygen from contacting with the anode fuel or catalyst thereby inhibiting NO_x formation. In this work we report a comparison of gadolinium and gadolinium-praseodymium doped barium cerate proton conducting solid electrolyte for an intermediate temperature fuel cell directly fed with ammonia.

2. Experimental

Doped barium cerate ($\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-x}$ (BCG) and $\text{BaCe}_{0.8}\text{Gd}_{0.19}\text{Pr}_{0.01}\text{O}_{3-x}$ (BCGP)) was prepared by conventional solid-state synthesis techniques. Appropriate stoichiometric ratios of high purity oxide powders (BaCO_3 , CeO_2 , Gd_2O_3 and Pr_6O_{11}) were ground, mixed and then ball milled in isopropyl alcohol for 24 h. The dried powders were subsequently calcined at 1350°C in air for 10 h. The calcined powder was mixed with a 15% polyvinyl alcohol solution and uniaxially pressed at 65 MPa into approximately 3 cm diameter and 2 mm thick pellets. The samples were subsequently isostatically pressed at 275 MPa. The discs were then sintered at 1600°C for 10 h and ground and polished to approximately 1.3 mm thickness. Planar single element fuel cells were fabricated utilizing Engelhard platinum ink A-4338 for the anode and cathode. The Pt electrodes were air dried and then fired at 1000°C for 1 h in air, with heating and cooling rates of 5°C min^{-1} .

The discs were installed between two nickel alloy plates which are compressed by a spring-loaded rod to prevent any displacement and provide an adequate seal. The plates had machined recessed surfaces, 1 mm deep \times 2 cm diameter to form the anode and cathode chambers, and welded stainless steel tubes to deliver gases to the chambers. Gas compositions were measured by an HP 5890 gas chromatograph (GC). The reactor was heated to 700°C at a ramp of 3°C min^{-1} while gas flows of $50\text{ cm}^3\text{ min}^{-1}$ of hydrogen and air were supplied at the anode and cathode respectively.

3. Results and discussion

A representation of the operating fuel cell is shown in Fig. 1. Ammonia is decomposed into nitrogen and hydrogen at the anode chamber. Protons generated at the anode are transported through the ceramic electrolyte to the cathode. Oxygen ions are electrochemically generated at the cathode and react with the protons from the anode. The removal of hydrogen from the anode chamber drives the equilibrium limited decomposition reaction to completion. The resistive heat generated by the oxidation of hydrogen also provides energy for the endothermic ammonia decomposition reaction.

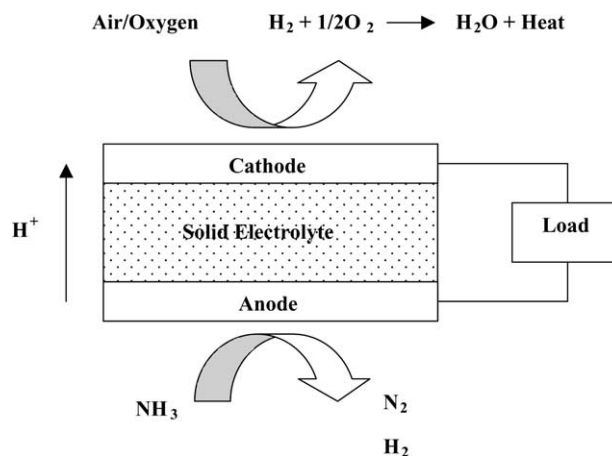


Fig. 1. Schematic representation of an ammonia fuel cell using a proton conducting electrolyte.

Fig. 2 depicts the relation between the oxygen flow in the cathode chamber and the amount of current produced by the cell. As the current is increased, more oxygen is consumed by the combustion reaction with hydrogen, thereby reducing the oxygen concentration in the outlet gas of the cathode. Oxygen concentrations of the outlet cathode gas, at various currents, were measured by gas chromatography (GC). Oxygen variations measured by GC are in accordance with predicted variations calculated from the electronic data. This correlation confirms that experiments were operated under a closed system with minimal effects due to leaks.

Gadolinium doped barium cerate (BCG) solid electrolyte discs of approximately 2 cm^2 area and 1.3 mm thickness were tested at 700°C . Initially, tests were performed under $50\text{ cm}^3\text{ min}^{-1}$ of hydrogen to provide a comparative benchmark. The cell was kept under hydrogen for almost 80 h on stream without showing any signs of degradation or loss of performance. Table 1 shows the current generated by the cell at various times, while operating at close proximity to the optimal power density. Initial flow changes resulted in a slight decrease of current measurements. However, the effect

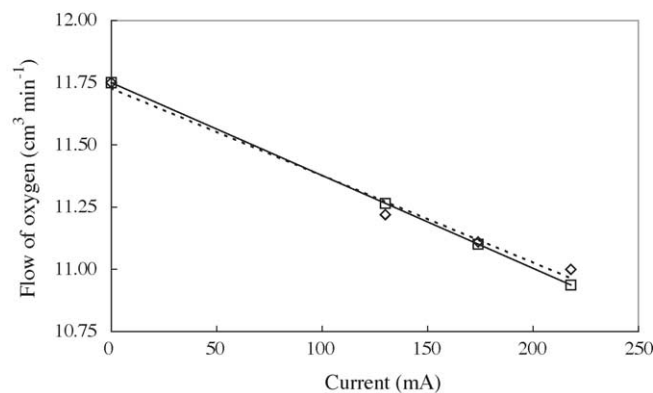


Fig. 2. Oxygen concentration at the cathode outlet as a function of cell current. Flow of oxygen (□) calculated from electronic data, and (◇) measured by gas chromatograph.

Table 1
Measured current of BCG electrolyte fuel cell under hydrogen at various times

Time on stream (h)	Current (mA)	Flow ($\text{cm}^3 \text{min}^{-1}$)	
		Hydrogen	Air
6	153	25	25
30	153	25	25
54	141	15	15
78	148	15	15
78	155	25	25

Hydrogen and air feed rates were varied. Temperature was kept at 700°C

is reversible since currents return to initial levels as the original flow rates are reintroduced.

Subsequently, various rates of ammonia were fed to the anode. Fig. 3 shows the voltage and current data collected under both hydrogen and ammonia fuels. Cell voltages at given currents were only slightly lower under ammonia feeds compared to pure hydrogen. The marginal difference can be attributed to a lower partial pressure of hydrogen caused by the production of nitrogen when ammonia is decomposed. Additionally, we notice a subtle effect when ammonia flow rates are lowered. Decreasing ammonia feed rates results in an increase of hydrogen utilization. This causes the ratio of nitrogen to hydrogen at the anode to increase and thus cell voltage to decrease.

Under direct ammonia feed, BCG electrolytes yielded an optimal power density of 25 mW cm^{-2} at a current density of 50 mA cm^{-2} . A comparative test was run using a gadolinium and praseodymium-doped barium cerate (BCGP) electrolyte. The power density data comparing both materials are shown in Fig. 4. The doubly doped BCGP resulted in higher overall fuel cell performance, under both hydrogen and ammonia, when compared to the BCG material. As was the case with the BCG material, a slight decrease in performance characteristics was observed under direct ammonia feed with the doubly doped barium cerate. However, results at 700°C using ammonia indicate a definite improvement to the single doped barium cerate, since the BCGP yielded an

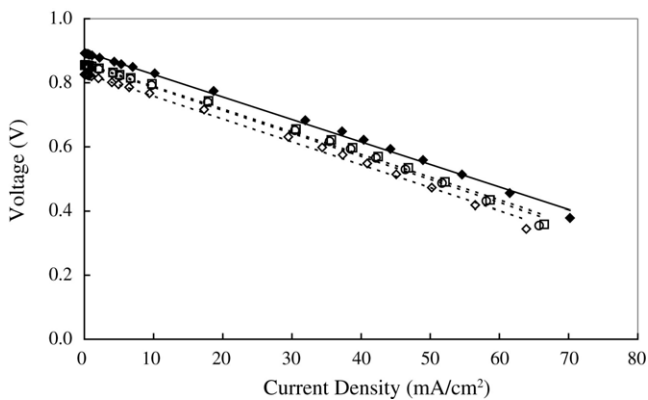


Fig. 3. J - V characteristics of 1.3 mm thick Gd-doped barium cerate electrolyte in hydrogen and ammonia at 700°C . (\blacklozenge) H_2 , $50 \text{ cm}^3 \text{min}^{-1}$; (\square) NH_3 , $40 \text{ cm}^3 \text{min}^{-1}$; (\circ) NH_3 , $25 \text{ cm}^3 \text{min}^{-1}$; (\diamond) NH_3 , $10 \text{ cm}^3 \text{min}^{-1}$.

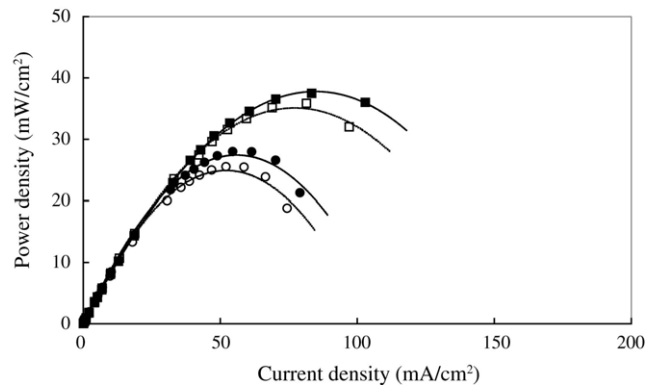


Fig. 4. Power density characteristics of Gd-doped, and Gd and Pr-doped barium cerate electrolytes in hydrogen and ammonia at 700°C . (\bullet) BCG, hydrogen; (\circ) BCG, ammonia; (\blacksquare) BCGP, hydrogen; (\square) BCGP, ammonia.

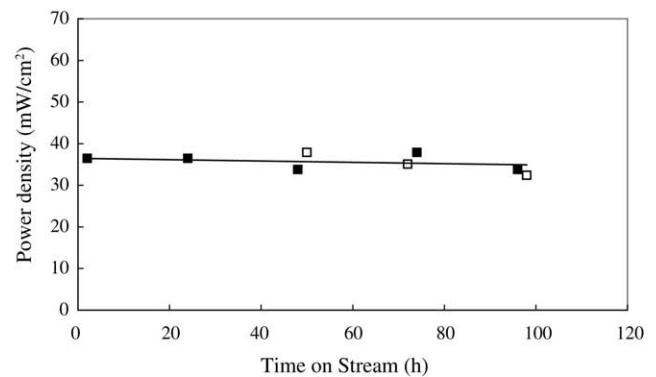


Fig. 5. Power density as a function of time on stream at 700°C . Fuel was alternated between (\blacksquare) hydrogen and (\square) ammonia.

optimal power density of 35 mW cm^{-2} at a current density of 75 mA cm^{-2} .

Performance characteristics of the BCGP fuel cell were monitored for over 100 h on stream, while operating under alternating hydrogen/ammonia fuels. Fig. 5 shows the optimal power density of the working cell over time. The cell was kept under ammonia for periods of up to 24 h. The data indicates no sign of deterioration in performance as a result of operation in either hydrogen or ammonia. Results also show that the fuel to the anode can be frequently cycled between hydrogen and ammonia without observing a decrease in power density.

4. Conclusions

Single cell intermediate temperature direct ammonia fuel cells have been successfully demonstrated at 700°C using proton conducting Gd-doped barium cerate (BCG) or doubly doped barium cerate electrolyte containing Gd and Pr (BCGP). Fuel cell performance using BCGP electrolyte was enhanced by about 40% over BCG electrolyte in either hydrogen or direct ammonia feed. A fuel cell using BCGP electrolyte showed no measurable degradation

in performance for over 100 h in alternating hydrogen and ammonia feed.

Acknowledgment

The authors acknowledge funding for this project from the Office of Energy Research and Development (OERD) at Natural Resources Canada.

References

- [1] S.E. Gay, M. Eshani, Fuel Cells: Technology, Alternative Fuels and Fuel Processing, SAE International, Warrendale, PA, 2003.
- [2] R. Metkemeijer, P. Achard, Int. J. Hydrogen Energy 19 (1994) 535–542.
- [3] R. Metkemeijer, P. Achard, J. Power Sources 49 (1994) 271–282.
- [4] M. Powell, A. Chellappa, Ammonia-based hydrogen generation for fuel cell power supplies, in: Proceedings of the 23rd Army Science Conference, Orlando, FL, USA, 2002.
- [5] M. Cifrain, K. Kordesch, J. Power Sources 127 (2004) 234–242.
- [6] H. Andersen, Large scale hydrogen production with CO₂ capture and sequestration, in: Proceedings of the 14th World Hydrogen Energy Conference, Montreal, Canada, 2002.
- [7] R.D. Farr, C.G. Vayenas, J. Electrochem. Soc. 127 (1980) 1478.
- [8] A. Wojcik, H. Middleton, I. Damopoulos, J. Van Herle, J. Power Sources 118 (2003) 342.
- [9] A. McFarlan, L. Pelletier, N. Maffei, J. Electrochem. Soc. 151 (2004) 930–932.
- [10] H. Iwahara, T. Esaka, H. Uchida, N. Maeda, Solid-State Ionics 3–4 (1981) 359.
- [11] K. Katahira, Y. Kohchi, T. Shimura, H. Iwahara, Solid-State Ionics 138 (2000) 91.